

LAMINATED METAL SHEET AND METHOD OF PRODUCTION OF SAME

## 5 TECHNICAL FIELD

The present invention relates to a laminated metal sheet used as a material for food cans and other containers and comprised of a metal sheet laminated on the front and back with two types of resins with  
10 different melting points and a method of production of the same.

## BACKGROUND ART

As materials for food cans, beverage cans, aerosol cans, and other containers, metal sheets covered on their  
15 surfaces with a polyester, polyolefin, or other thermoplastic resin are being made much use of. In this case, the metal sheet used is generally steel sheet or aluminum sheet. Among these, for example, polyester-based resins are generally superior in corrosion resistance,  
20 flaw resistance, and printability and can be used for both the inner surface and outer surface of cans in some cases, but when the content is alkaline, the resin is insufficient in durability. Further, when used for meat-based food cans, there is the problem that the meat  
25 releasability is poor. To solve this problem, two-sided laminated metal sheets covered with different types of resin at the can inside surface side and the can outer surface side are being used.

In general, as the can outer surface side film, a  
30 relatively hard polyester-based resin film is preferably used, while as the can inside surface side film, a lower melting point, excellent meat releasability and alkali durability, relatively soft polyolefin-based resin film is preferably used. Metal sheet laminated with different  
35 films on its two surfaces is disclosed in Japanese Patent Publication (A) No. 63-231926, Japanese National Publication (A) No. 2-501644, and Japanese Patent

EV 320 248 660 US

Publication (A) No. 2002-120324. Note that the terms "high melting point film" and "low melting point film" used in the present description do not mean films with melting points of absolute values. A relatively high melting point side film is called a "high melting point film", while a relatively low melting point side film is called a "low melting point film".

In general, a laminated metal sheet is produced by the method of superposing a heated metal sheet and resin films and using lamination rolls to apply pressure to bond them (heat lamination method). To make them bond, the temperature of a film surface contacting the metal sheet has to be at least its melting start point  $T_{sm}$  (normally a temperature about 0 to 30°C lower than the melting point), more preferably at least the melting point MP, but on the other hand if the temperature of a film surface contacting a lamination roll becomes the melting start point or more, the film will stick to the lamination roll making production impossible.

For this reason, the temperature of the metal sheet at the lamination part has to be strictly controlled in relation with the film melting points, but when using a polyester-based resin film as the high melting point film and using a polyolefin-based resin film as the low melting point film, since the melting points MP of the two greatly differ (for example, polyethylene terephthalate (polyester-based) has a melting point of 265°C, while polypropylene (polyolefin-based) has one of 168°C), there is the problem that if setting the temperature of the metal sheet to match with one of the films, the other film will not bond well.

Therefore, as shown in Japanese Patent Publication (A) No. 63-231926, the method of first laminating the high melting point resin film, then laminating the low melting point resin film in a later step where the temperature of the metal sheet falls, that is, a two-step

lamination method, and, as shown in Japan National  
Publication (A) No. 2-501644, the method of reheating  
after the lamination step by the press-bonding of the  
lamination rolls so as to melt-bond the resins have been  
5 proposed, but both of these have the problems of swelling  
capital costs. Further, Japanese Patent Publication (A)  
No. 2002-120324 proposes a simultaneous lamination method  
matching the temperature of the metal sheet with the low  
melting point resin film, but it is believed that a low  
10 melting point resin for bonding purposes is required at  
the metal sheet side of the high melting point resin  
film, so again the cost rises.

Further, in the prior art disclosed in Japanese  
Patent Publication (A) No. 63-231926 and Japanese Patent  
15 Publication (A) No. 2002-120324, since the low melting  
point resin film is kept from melt-bonding with the  
lamination roll by setting the temperature of the metal  
sheet to match with the low melting point resin film, the  
crystallization degree will not be lowered to an extent  
20 enabling the laminated low melting point resin film to be  
sufficiently worked. For this reason, when bending a two-  
sided laminated metal sheet to work it to a food can  
etc., the phenomenon of the worked part of the low  
melting point film whitening appears. It looks like the  
25 can contains foreign matter. Therefore, users and can  
makers would be liable to raise complaints.

#### DISCLOSURE OF THE INVENTION

The present invention solves the above problems of  
the prior art and provides a laminated metal sheet  
30 enabling simultaneous lamination of two types of film  
with different melting points, without sticking on the  
lamination rolls, on the two surfaces of a metal sheet  
and a method of production of the same. Further, the  
present invention provides more inexpensively a two-sided  
35 laminated metal sheet free from the low melting point  
resin film whitening even when working the sheet to  
produce a food can etc. The present invention has as its

gist the following.

(1) A laminated metal sheet obtained by laminating two types of film including a high melting point film and low melting point film on the two sides of a metal sheet, said laminated metal sheet characterized by having a low melting point film thickness  $d_2$  defined by the following equation 1:

$$d_2 (\mu\text{m}) \geq k (\Delta\text{MP} - \Delta T) / V$$

where,  $\Delta\text{MP} = \text{MP1} - \text{MP2}$

MP1: melting point of high melting point film  
(°C)

MP2: melting point of low melting point film

(°C)

k: constant determined by low melting point film's heat conductivity, heat capacity, and temperature,  
 $k \geq 2 [\mu\text{m} \cdot \text{m} / (\text{°C} \cdot \text{s})]$

$$0 < \Delta T = \text{MP1} - \Phi \cdot T_i \leq 50 (\text{°C})$$

$T_i$ : metal sheet temperature at lamination roll inlet side (°C)

$\Phi$ : constant determined by heat removal conditions at time of lamination ( $0.75 \leq \Phi < 1$ )

V: sheet running speed (m/s)

(2) A laminated metal sheet as set forth in (1), characterized in that said high melting point film is comprised of a polyester-based resin and said low melting point film is comprised of a polyolefin-based resin.

(3) A laminated metal sheet as set forth in (2), characterized in that said polyester-based resin is selected from polyethylene terephthalate, a polyethylene terephthalate/isophthalate copolymer, polyethylene naphthalate, a polyethylene terephthalate/naphthalate copolymer, a mixed resin of polybutylene terephthalate and polyethylene terephthalate, a mixed resin of polybutylene terephthalate and a polyethylene terephthalate/isophthalate copolymer, and further one of these resins including a pigment or dye.

(4) A laminated metal sheet as set forth in (2), characterized in that said olefin-based resin is selected from a polypropylene, polyethylene, a polypropylene/polyethylene random copolymer, or these resins including a pigment or dye.

(5) A laminated metal sheet as set forth in (1), characterized in that a difference  $\Delta H_z$  between a haze value  $H_z2$  of a low melting point film after bending a sheet of a thickness of 1 mm by 180 degrees across said high melting point film side and a haze value  $H_z1$  of the low melting point film before bending is made not more than 20%.

(6) A laminated metal sheet as set forth in (5), characterized in that the haze value  $H_z1$  of the low melting point film before bending is made not more than 60%.

(7) A laminated metal sheet as set forth in (1) or (2), characterized by using for said high melting point film a biaxially stretched polyester-based resin film and leaving crystal orientation at that surface layer.

(8) A laminated metal sheet as set forth in (1), characterized in that, among the two types of film including said high melting point film and low melting point film, when the melting points inside the films differ according to the position in the thickness direction, the lower surface melting point of the one film at the side contacting the roll is designated as MP2 and the film melting point of the other film at the metal sheet side is designated as MP1 for calculation and lamination.

(9) A laminated metal sheet as set forth in (8), characterized in that the sheet running speed  $V$  defined in (1) is made 1 to 3.5 m/s for lamination.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an enlarged sectional view of a two-sided laminated metal sheet of the present invention.

FIG. 2 is an explanatory view of a process of

production of a two-sided laminated metal sheet.

FIG. 3 is a view of the temperature profiles immediately before the rolls separate from the films in the case of laminating same melting point films on the two sides of a metal sheet.

FIG. 4 is a graph of a heat conduction analysis model.

FIG. 5 is a graph of temperature gradients inside the two types of film.

FIG. 6 is a graph of a method for finding a thickness by which a film will not stick to the rolls.

FIG. 7 is a view of the temperature profiles at the lamination roll exit side in the present invention.

FIG. 8 is an explanatory view of bending by 180 degrees.

FIG. 9 is a perspective view of an easy peel EOE.

#### BEST MODE FOR WORKING THE INVENTION

FIG. 1 is an enlarged sectional view of a two-sided laminated metal sheet of the present invention, wherein 3 indicates a steel sheet, aluminum sheet, or other metal sheet, 1 a high melting point film laminated at one side of this metal sheet 3, and 2 a low melting point film laminated at the other side of this metal sheet 3.

FIG. 2 is an explanatory view of a process of production of a two-sided laminated metal sheet according to the present invention. In FIG. 2, 10 indicates a pair of left and right lamination rolls. A high melting point side film 1 and a low melting point side film 2 are superposed over the two sides of the metal sheet 3 and press bonded by the lamination rolls 10. The metal sheet 3 is for example a steel sheet. In the case of use as a material for a container, the metal sheet 3 has a thickness of 0.1 to 0.5 mm or so in usual cases. The high melting point side film 1 is, for example, a relatively hard, superior printability, flaw resistance, retort bondability, etc. polyester-based resin, while the low melting point side film 2 is, for example, a superior

corrosion resistance, workability, meat releasability, retort bondability, etc. polyolefin-based resin. Note that A indicates a point immediately before the metal sheet 3 and films contact, while B indicates a point immediately before the films separate from the lamination rolls 10.

In the present invention, the metal sheet 3 is heated in advance to a temperature at least the melting start point of the high melting point side film 1, preferably the melting point+50°C or less, for example, 270°C. As a result, both the film 1 and the film 2 are raised in temperature at the sides contacting the metal sheet 3 to at least the melting start points and bond with the metal sheet 3. At this time, both the films 1 and 2 rise in temperature at the opposite sides (sides contacting the lamination rolls 10) due to conduction of heat from the metal sheet 3, but the film 1 can generally be bonded under conditions where the roll exit side metal sheet temperature  $T_d (= \Phi \cdot T_i, \Phi$  being a constant determined by the heat removal conditions at the time of lamination,  $0.75 \leq \Phi < 1$ ) is less than the melting start point of the film 1, so under those conditions, will not stick to the lamination roll 10.

FIG. 3 schematically shows, for explanatory purposes, the temperature profiles inside the metal sheet and films immediately before the rolls separate from the films in the case where the same melting point films are bonded to the two sides of the metal sheet 3. The temperature of the metal sheet  $T_i$  at the point A immediately before the metal sheet and the films are brought into contact by the rolls becomes higher than the melting start point  $T_{sm1}$  of the films, but the temperature of the metal sheet  $T_d (= \Phi \cdot T_i)$  at the point B immediately before the rolls separate from the films usually becomes lower than the melting start point  $T_{sm1}$  of the films. Therefore, the temperatures of the film

surfaces at this point of time become lower than the melting start point  $T_{sm1}$  of the films and the films will not stick to the rolls 10.

Usually, each film has a thickness determined by the reason that for example the lower limit of film formation is 10  $\mu\text{m}$  or that for corrosion resistance to be maintained, 20  $\mu\text{m}$  or more is necessary. By selecting the lamination conditions in accordance with the determined thickness, it is possible to avoid sticking. The conditions under which a film will not stick to a roll are conditions where, while the roll and film are in contact, the temperature at the point C of the film thickness position is less than the melting start point  $T_{sm1}$ . This can be achieved by selecting the lamination conditions. Specifically, when laminating two types of film with different melting points on a metal sheet, if considering corrosion resistance in food can applications, the high melting point side film generally has a thickness of 20 to 30  $\mu\text{m}$  or so, but greater thicknesses can be obtained for other applications.

Further, the temperature of the metal sheet when contacting the films normally becomes higher than the melting start point  $T_{sm1}$  of the films, but at the point of time when the rolls separate from the films, as shown in FIG. 3, it becomes lower than the melting start point  $T_{sm1}$  of the films. This is because heat is removed through the film to the roll side. If considering the fact that the temperature ( $T_i$ ) at the point A immediately before the metal sheet and films contact is higher than the melting start point  $T_{sm1}$  of the films, by experience, as shown in equation 1,  $0 < MP1 - T_d = MP1 - \Phi \cdot T_i \leq 50$  ( $^{\circ}\text{C}$ ) becomes required as a condition. That is, if  $MP1 - \Phi \cdot T_i$  becomes 50 $^{\circ}\text{C}$  or more,  $T_i$  becomes  $T_{sm1}$  or less and bonding is sometimes not sufficient. This condition becomes a required condition of the roll inlet side temperature for bonding the high melting point film to a metal sheet when



laminating two types of film with different melting points. Note that  $\Phi$  is determined by the heat removal conditions at the time of lamination and specifically is determined by adjusting the lamination rolls in surface temperature or pressing force.  $\Phi < 1$ . In general,  $0.75 \leq \Phi < 1$  can be adjusted to.

Further, the higher the temperature  $T_i$  at which the metal sheet and films are bonded, the better the bondability of the metal sheet and the high melting point film. If raising  $T_i$ ,  $T_d (= \Phi \cdot T_i)$  also becomes higher, so to further raise the bondability, by experience, it is sufficient to set  $T_i$  about  $10^\circ\text{C}$  higher than the bonding lower limit temperature. This can generally be achieved if  $0 < MP_1 - \Phi \cdot T_i \leq 40$  or so. By raising the film bondability, the film peeling strength, corrosion resistance, retort bondability, etc. can be improved.

When laminating the high melting point film 1 and low melting point film 2, if applying lamination conditions commensurate with the melting point of the film 1 without considering the film thickness, due to the heat conduction from the metal sheet 3, the temperature of the film 2 at the side contacting the lamination roll 10 will exceed the melting start point of the film 2 and the film will end up sticking to the lamination roll 10 in some cases. However, in the present invention, the low melting point side film is adjusted in thickness  $d_2$  to specifically make  $d_2 \geq k (\Delta MP - \Delta T) / V$  and thereby solve this problem. Here,  $\Delta MP = MP_1 - MP_2$ , where  $MP_1$  is the melting point ( $^\circ\text{C}$ ) of the high melting point film,  $MP_2$  is the melting point ( $^\circ\text{C}$ ) of the low melting point film, and  $V$  is the sheet running speed (m/s). Further,  $\Delta T = MP_1 - \Phi \cdot T_i$ .

Here,  $k$  is a coefficient expressed by equation 2 according to the Law of Heat Conduction:

$$k = \frac{\lambda_2 L}{Cp_2 \cdot \alpha}$$

Below, the content of equation 2 will be explained.

5 First, as shown in FIG. 4, a one-dimensional heat conduction analysis model of the inside of a film having an abscissa  $x$  indicating the film thickness and an ordinate indicating the temperature  $T$  is prepared. The temperature when  $x=0$  is the temperature of the metal sheet at a certain time  $t$ . Further, if the temperature of the side of the film contacting the roll is less than the melting start point  $T_{sm1}$ , it is assumed that the film will not stick to the roll. The distance  $d$  not sticking to the roll becomes the necessary film thickness.

15 In the present invention, two types of film are laminated on the metal sheet, so, as shown in FIG. 5, two curves are shown, but the heat conductivities  $\lambda$  and the specific heat  $Cp$  do not greatly differ (seldom differ by an order of magnitude), so the distance  $x$  is divided by  $\lambda$  and the result multiplied with  $Cp$  to obtain a parameter and the two curves are approximated as the single curve as shown in FIG. 6. Further, in FIG. 6, by finding the coordinates  $(dCp/\lambda)_1$  and  $(dCp/\lambda)_2$  of the intersections of the horizontal lines drawn from  $T_{sm1}$  and  $T_{sm2}$  and this curve, multiplying these values with  $\lambda_1$  ( $\lambda_2$ ), and dividing by  $Cp_1$  ( $Cp_2$ ), the thicknesses  $d_1$  and  $d_2$  sticking to the rolls can be calculated.

If approximating the curve of FIG. 6 by a straight line, it is expressed by  $T=A-B (Cpx/\lambda)$ . When  $x=0$ ,  $T=T_d=\Phi \cdot T_i=A$ , so  $T=\Phi \cdot T_i-B (Cpx/\lambda)$ . Therefore, to prevent roll sticking,  $\Phi \cdot T_i-B (Cpx/\lambda) \leq T_{sm}$ , therefore,  $x \geq \lambda / (Cp \cdot B) (\Phi \cdot T_i - T_{sm})$ . Right now the problem is the conditions under which the low melting point side film will not stick to the roll, so  $d_2 \geq \lambda_2 / (Cp_2 \cdot B) (\Phi \cdot T_i - T_{sm2})$ .

35 The time  $t$  is the contact time, so  $t=L/V$  ( $V$  is the

sheet running speed, and  $L$  is the contact length). If considering the fact that the inclination  $B$  is inversely proportional to the contact time (when the contact time becomes longer, the temperature becomes even),  $B = \alpha (V/L)$ .

5 Therefore,  $d_2 \geq \lambda_2 \cdot L / (Cp_2 \cdot \alpha \cdot V) (\Phi \cdot Ti - T_{sm2})$ . If  $\lambda_2 \cdot L / (Cp_2 \cdot \alpha) = k$ , then  $d_2 \geq k (\Phi \cdot Ti - T_{sm2}) / V$ .

This  $d_2 \geq k (\Phi \cdot Ti - T_{sm2}) / V$  is substantially equivalent to  $d_2 \geq k (\Delta MP - \Delta T') / V$  from the relationships  $T_{sm1} - T_{sm2} \cong MP_1 - MP_2 = \Delta MP$  and  $\Delta T' = T_{sm1} - \Phi \cdot Ti$ . Since  $\Delta T = MP_1 - \Phi \cdot Ti \geq \Delta T'$ ,  $d_2 \geq k$   
10  $(\Delta MP - \Delta T') / V \geq k (\Delta MP - \Delta T) / V$ . As shown in FIG. 7, this expresses the conditions for maintaining the temperature of the low melting point side film 2 at the side contacting the lamination roll 10 at less than the melting point of the film 2. Note that in FIG. 3, a  
15 simplified temperature gradient is shown, but the time during which the films 1 and 2 pass the lamination rolls 10, 10 is a short time of several tens of msec. Nonconstant heat movement occurs, so accurate analysis of the actual heat movement phenomenon is extremely  
20 difficult. Further, the pressing forces of the rolls, the surface conditions of the films, etc. cause the state of contact of the metal sheet and films and the films and roll to change. Due to this, the films also change in surface temperatures, so the temperature gradient also  
25 changes. Therefore, when finding the range of the value of  $k$  based on the Law of Heat Conduction operatively, it was learned that the range was  $k \geq 2$ . The larger the value of  $k$ , the greater the effect of suppression of film sticking, but actually 5 or so is sufficient.

30 Here, the method of finding  $d_2$  will be explained again.

1) Two types of film are selected.

2) The low melting point side  $MP_2$ ,  $\lambda_2$ , and  $Cp_2$  are investigated.

35 3) The high melting point side  $MP_1$  and  $\lambda_1$  are

investigated.

(If there are results of normal operation,  $\lambda_1$  and  $C_p$  may be unknown)

4) The value of  $T_i$  and the conditions of  $\Phi$  are found  
5 from MP1.

Normally, when  $MP1 - \Phi \cdot T_i = \Delta T$ ,  $\Delta T \leq 50^\circ\text{C}$ .

5)  $d_2$  is found from  $d_2 \geq k(\Delta MP - \Delta T)/V$ .

In this case, the minimum value of  $d_2$  is when  $k=2$ .  
This value is determined with reference to  $\lambda_2$  and  $C_{p2}$  of  
10 the low melting point film 2 and the operating  
conditions. Note that the value of  $d_1$  is determined by  
the corrosion resistance and other functions.

Further, according to the above formula, if making  
the sheet running speed  $V$  greater, the films can be made  
15 thinner in thickness  $d_2$ , but for the runnability of the  
films or the uniform heating of the metal sheet, it is  
not preferable that the sheet running speed  $V$  be made  
that high. Normally, the operation is performed at 2.5 to  
3.5 m/s or so. However, depending on the facility, it is  
20 of course possible to make the value one over 3.5 m/s. As  
the metal sheet, various types of metal generally used as  
container materials such as aluminum sheet, soft steel  
sheet, various types of plated steel sheet, stainless  
steel sheet, etc. may be used.

25 The resin forming the high melting point film 1 may  
in principle be any thermoplastic resin. Ones selected  
from polyethylene terephthalate, polyethylene  
terephthalate/isophthalate copolymer, polyethylene  
naphthalate, polyethylene terephthalate/naphthalate  
30 copolymer, a mixed resin of polybutylene terephthalate  
and polyethylene terephthalate, a mixed resin of  
polybutylene terephthalate and a polyethylene  
terephthalate/isophthalate copolymer, or these resins  
including a pigment or dye are frequently used. Normally,  
35 for increasing the strength or hardness, a biaxially  
stretched film is used.

Further, for the purpose of increasing the bondability, it is also possible to give the metal sheet surface a chromate coating, give the surface of the resin contacting the steel sheet an adhesive layer having polarity, etc. in combination.

On the other hand, the resin forming the low melting point film 2 may in principle be any thermoplastic resin. Resins selected from polypropylene, polyethylene, a polypropylene/polyethylene random copolymer, or these resins including a pigment or dye are frequently used. These polyolefin-based resins are lower in melting point compared with the polyester-based resin forming the high melting point film 1. For example, the polyethylene terephthalate resin used as the high melting point film 1 has a melting point of 265°C, while the polypropylene resin used as the low melting point film 2 has a melting point of 168°C.

In the above way, the two-sided laminated metal sheet of the present invention is one in which the low melting point film 2 is adjusted in thickness to become thicker and is simultaneously laminated under relatively high temperature conditions matching the temperature conditions of the metal sheet 3 with the high melting point film 1. As a result, the laminated low melting point film 2 is heated to a considerably higher temperature than the conventional two-sided laminated metal sheet and becomes amorphous.

For this reason, the two-sided laminated metal sheet of the present invention becomes resistant to whitening even when bending for working it into a container etc. Clarifying this point by numerical values, in the present invention, as shown in FIG. 8, a sheet 4 having a thickness of 1 mm is bent 180 degrees to the outside across the high melting point film 1 side. The whitenesses of the low melting point film 2 before and after this are defined by the haze values. That is, the bending work is 180 degree bending so that the low

melting point film 2 becomes the outside.

The haze value is the value defined as the diffusion transmittance/total light transmittance x 100 (%) when optically measuring the haze value of the film. The measurement method is prescribed in JIS-K7136. Here, the two-sided laminated metal sheet before bending and after bending is immersed in 40°C 18% HCl to make the metal sheet 3 dissolve, the low melting point film 2 is peeled off, then a 50 mm x 50 mm sample for measurement of the haze is taken so that the bent part becomes the center, the measurement is performed three times, and the average value is taken. The measurement is performed centered at the bent part.

The two-sided laminated metal sheet of the present invention has a difference  $\Delta H_z = H_{z2} - H_{z1}$  of not more than 20% when the haze value of the low melting point film 2 before bending is  $H_{z1}$  and the haze value after bending is  $H_{z2}$ . Further, the haze value  $H_{z1}$  of the low melting point film 2 before bending is preferably not more than 60%. By making this difference of the haze value  $\Delta H_z$  before and after bending not more than 20%, even when performing bending work etc. in the food can production process, the low melting point film 2 is free from whitening and the can no longer appears to contain foreign matter.

Note that the whitening at the time of the bending work is accompanied with the formation of microcracks, but if  $\Delta H_z$  is made not more than 20% as shown in the following examples, this problem can be avoided. Further, if the haze value  $H_{z1}$  of the low melting point film 2 before bending is over 60%, the inner surface of the can whitens in appearance, so this is not preferable.

In the above way, the two-sided laminated metal sheet of the present invention has a difference  $\Delta H_z$  of the haze values of the low melting point film 2 before and after bending of not more than 20% and can be produced by the low production cost simultaneous

lamination method. Further, the temperature conditions of the metal sheet 3 can be set matching with the characteristics of the high melting point film 1, so it is possible to use for the high melting point film a  
5 biaxially stretched polyester-based resin film and laminate it in the state with that surface layer having residual crystal orientation.

Note that when working the two-sided laminated metal sheet of the present invention into a container body, the  
10 high melting point film 1 is usually made the outside and the low melting point film 2 the inside. However, when using as the easy peel EOE (easy open end) shown in FIG. 9 or other can inside lid 5 the two-sided laminated metal sheet of the present invention, to raise the heat  
15 sealability with the outer lid 6 laminated with polypropylene at its bottom surface, sometimes the low melting point film 2 is used as the top side (can outer surface side). In this way, which side to make the outside of the container may be suitably determined in  
20 accordance with the application.

#### Example 1

The various types of film 1 (melting point MP1, thickness d1) and the various types of film 2 (melting point MP2, thickness d2) shown in Table 1 were laminated  
25 under the lamination conditions shown in Table 1 on the two sides of chrome plated steel sheets. Invention Examples 1 to 8 all had thicknesses d2 of the films 2 larger than the values of d2 calculated from the lamination conditions. The roll sticking of the films 2  
30 of the invention examples and the bondability of the films 1 to the steel sheet were evaluated. The results are shown in Table 2. Further, examples outside the conditions of the present invention are similarly shown as Comparative Examples 1 to 5 in Table 1 and Table 2.

35 Note that, in Table 1, PP shows polypropylene film, but pure PP is nonpolar and cannot sufficiently be bonded by heat lamination, so one giving the metal bonding

surface side a modified PP adhesive layer (melting point 166°C) having a thickness of 4  $\mu\text{m}$  and polarity is used. Further, the polyethylene film shown as PE is also nonpolar and cannot be sufficiently bonded by heat lamination in the pure state, so one giving the metal bonding surface side an ethylene acrylate copolymer resin adhesive layer (melting point 99°C) of a thickness of 10  $\mu\text{m}$  is used.



Table 1

No.		Film 1	MP1 °C	d1 µm	Film 2	MP2 °C	d2 µm	V m/s	Ti °C	Φ	ΦTi °C	d2 calculated value	
												k	µm
1	Inv. Ex. 1	PET-IA*5	226	20	PP*7	168	40	2.5	233	0.858	200	2	25.5
2	Inv. Ex. 2	PET-IA*5	226	20	PP*7	168	25	2.9	233	0.858	200	2	22.0
3	Inv. Ex. 3	PET-IA*5	226	20	PE*8	112	80	2.5	257	0.778	200	2	70.4
4	Inv. Ex. 4	PET*6	265	13	PP*7	168	70	2.5	285	0.842	240	2	57.6
5	Inv. Ex. 5	PET-IA*5	226	13	PP*7	168	85	2.5	226	0.931	210	5	84.8
6	Inv. Ex. 6	PP*7	168	20	EAA*	99	65	1	173	0.751	130	2	61.8
7	Inv. Ex. 7	PET*6	265	20	PP*7	168	40	3.5	271	0.849	230	2	35.5
8	Inv. Ex. 8	2-layer PET	226	13	PP*7	168	30	2.5	234	0.855	200	2	25.7
9	Comp. Ex. 1	PET-IA*5	226	20	PP*7	168	25	2.5	233	0.858	200	2	25.5
10	Comp. Ex. 2	PET-IA*5	226	20	PP*7	168	20	2.5	203	0.862	175	2	5.6
11	Comp. Ex. 3	PET-IA*5	226	20	PP*7	168	20	2.5	245	0.922	226	2	46.3
12	Comp. Ex. 4	PET-IA*5	226	20	PE*8	112	60	2.5	257	0.778	200	2	70.4
13	Comp. Ex. 5	PET*6	265	13	PP*7	168	40	2.5	285	0.842	240	2	57.6

\* EAA: ethylene acrylate copolymer

Table 2

No.		Film 2 roll sticking	Film 1 bondability	Remarks
1	Inv. Ex. 1	OK	OK	Plenty of leeway
2	Inv. Ex. 2	OK	OK	Increase of speed avoids sticking to lamination roll
3	Inv. Ex. 3	OK	OK	Change of type of film
4	Inv. Ex. 4	OK	OK	Change of type of film
5	Inv. Ex. 5	OK	OK	k practical upper limit
6	Inv. Ex. 6	OK	OK	V=1.0m/s
7	Inv. Ex. 7	OK	OK	V=3.5m/s
8	Inv. Ex. 8	OK	OK	2-layer structure
9	Comp. Ex. 1	NG	OK	Film sticking limit
10	Comp. Ex. 2	OK	NG	High temperature side bonding limit
11	Comp. Ex. 3	NG	OK	$\Phi T_i = MP_1$
12	Comp. Ex. 4	NG	OK	Change of type of film
13	Comp. Ex. 5	NG	OK	Change of type of film

According to Invention Example 1, even when performing retort processing in steam at 125°C x 30 minutes, a good bondability free from film peeling is obtained. Comparative Example 1 is an example in which the other conditions are made the same as in Invention Example 1, but the thickness of the film 2 is made 25  $\mu\text{m}$  or smaller than the 25.5  $\mu\text{m}$  of the calculated value of d2 and sticking to the lamination roll occurred. Therefore, an example in which the other conditions are made the same, but the sheet running speed of Comparative Example 1 is raised to 2.9 m/s is Invention Example 2. Due to this, the calculated value of d2 becomes 22  $\mu\text{m}$  or less than the 25  $\mu\text{m}$  of the thickness of the film 2. As a result, sticking to the lamination roll can be avoided.

Comparative Example 2 is an example of lowering  $T_i$  to  $T_d = \Phi T_i = 175^\circ\text{C}$  and as a result making  $\Delta T = MP_1 - \Phi T_i$  51°C. In this case, bonding is no longer possible. Further, Comparative Example 3 is an example in which  $\Phi T_i$  is raised to 226°C or equal to the melting point  $MP_1$  of the film 1. The film 2 stuck to the lamination roll.

Invention Example 3 is an example of changing the type of the film 2 from Invention Example 1 to PE. A laminated metal sheet was produced without allowing sticking to the lamination rolls. Comparative Example 4 is an example in which the conditions were made the same

as in Invention Example 3 and the thickness of the film 2 was made 60  $\mu\text{m}$  or thinner than the 70.4  $\mu\text{m}$  of the calculated value of d2. Sticking of the film 2 to the lamination roll occurred.

5           Comparative Example 5 is also an example in which the thickness of the film 2 was made 40  $\mu\text{m}$  or thinner than the calculated value of d2. Sticking of the film 2 to the lamination roll occurred. Therefore, in Invention Example 4, the other conditions were made the same as  
10 those of Comparative Example 5 and the thickness of the film 2 was made 70  $\mu\text{m}$ . As a result, the film no longer stuck to the lamination roll. Even if retort sterilizing the obtained laminated metal sheet, the film 1 did not peel.

15           Invention Example 5 is an example where the thickness of the film 2 is matched with the calculated value of d2. This is an example where the thickness of the low melting point film is close to the upper limit. If calculating the k value of this case utilizing the 85  
20  $\mu\text{m}$  thickness of the low density polyethylene film, about  $k=5$ . This extent of k value is believed to be the actual upper limit.

          Invention Example 6 is an example where even if the sheet running speed was made the lower limit of 1 m/s,  
25 lamination was possible without trouble. Further, Invention Example 7 is an example in which even if the sheet running speed is made the 3.5 m/s upper limit value of the facility, lamination was possible without trouble. Invention Example 8 is an example of use of a two-layer  
30 PET film as the film 1. This two-layer PET film is comprised of an outside of PET of a thickness of 7  $\mu\text{m}$  and a melting point of 265°C and an inside of PET-IA (\*5) of a thickness of 6  $\mu\text{m}$  and a melting point of 226°C.

          In the above invention examples and comparative  
35 examples, as the metal sheet, chrome plated steel sheet was used, but unplated steel sheet, aluminum sheet,

copper sheet, etc. treated on their surfaces as need give similar results as confirmed from experiments.

Note that \*1 to \*8 in the evaluation column of Table 1 show the following content.

5           \*1: Ia/Ib is the ratio of the following two peaks  
obtained by X-ray diffraction measurement using CuK $\alpha$ -rays  
at a two-sided laminated metal sheet at the high melting  
point film (polyester film) covered side. Ia is the X-ray  
diffraction intensity of the diffraction face of the  
10 (100) face parallel to the surface of the polyester film  
(distance between faces about 0.34 nm), while Ib is  
similarly the X-ray diffraction intensity by the  
diffraction face of the (110) face (distance between  
faces about 0.39 nm). In the examples, Ia/Ib is 0.7 to 10  
15 in range and shows that the crystal orientation remains  
without complete melting up to the surface layer.

          \*2: The corrosion resistance after working is the  
result from punching a two-sided laminated metal sheet  
into a disk shape of a diameter of 158 mm, drawing it by  
20 a draw ratio of 1.56 so that the low melting point film  
becomes the inner surface to obtain a shallow drawn cup,  
then redrawing it by a draw ratio of 1.23 to obtain a can  
of a cup diameter of 82 mm and a cup height of 52 mm (DRD  
can), filling the inside with 2% citric acid, then  
25 storing it at 37 degrees for six months and examining the  
inside surface of the can for the state of corrosion.

          \*3: PET-PBT is a mixed resin of polyethylene  
terephthalate and polybutylene terephthalate.

          \*4: Two-layer PET is two-layer structure film with a  
30 surface layer of 10 $\mu$ m PET (MP 265°C) and a bottom layer of  
10 $\mu$ m PET-IA (MP about 150°C).

          \*5: PET-IA is polyethylene  
terephthalate/isophthalate copolymer.

          \*6: PET is polyethylene terephthalate.

35           \*7: PP is polypropylene.

          \*8: PE is polyethylene.

Example 2

Table 3 shows examples of the present invention. The two types of films of the materials shown in the table were simultaneously laminated on the two sides of steel sheets. MP1 indicates the melting point of the high melting point film, d1 indicates its thickness, MP2 indicates the melting point of the low melting point film, and d2 indicates its thickness. The sheet temperature  $T_i$  indicates the metal sheet temperature at the time of lamination, while the speed  $v$  indicates the sheet running speed at the time of lamination. Hz1 and Hz2 were measured by the method explained above based on JIS-K7136. Further, Table 4 shows comparative examples.

Table 3

Table 3			Can outer surface side				Can inside surface side			Sheet temp- erature Ti °C	Speed v m/s	Evaluation result						
			Material of film	MP1 (°C)	d1 (μm)	Material of film	MP2 (°C)	d2 (μm)	H21 %			H22 %	ΔHz %	PET surface x-ray Ia/Ib*1	Form- ability	Can inside surface whitening	Corrosion resistance after working*2	
Inv. Ex. 9	PET-IA*5	226	20	PP *7	168	30	225	3.5	28.9	32.8	3.9	2.6	Good	Very good	No abnormality			
Inv. Ex. 10	PET-IA*5	226	20	PP *7	168	25	233	2.9	29.5	38.9	9.4	1.5	Good	Very good	No abnormality			
Inv. Ex. 11	PET-IA*5	226	20	PP *7	168	30	226	2.9	27.6	43.5	15.9	4.6	Good	Very good	No abnormality			
Inv. Ex. 12	PET-PBT*3	214	12	PP *7	168	25	212	2.9	25.3	44.3	19	4.8	Good	Good	No abnormality			
Inv. Ex. 13	PET*6	265	20	PP *7	168	40	271	3.5	38.6	42.3	3.7	1.4	Good	Very good	No abnormality			
Inv. Ex. 14	PET-IA*5	226	20	PP *7	168	40	233	2.5	35.2	44.8	9.6	1.5	Good	Very good	No abnormality			
Inv. Ex. 15	PET-IA*5	226	13	PP *7	168	40	228	2.5	34.3	48.9	14.6	3.2	Good	Very good	No abnormality			
Inv. Ex. 16	PET-PBT*3	214	12	PP *7	168	40	216	2.5	32.6	50.2	17.6	3.9	Good	Good	No abnormality			
Inv. Ex. 17	PET-IA*5	226	20	PE*8	112	80	257	2.5	48.5	50.8	2.3	0.7	Good	Very good	No abnormality			
Inv. Ex. 18	PET*6	265	13	PP *7	168	70	285	2.5	46.2	55.9	9.7	1.2	Good	Very good	No abnormality			
Inv. Ex. 19	PET-IA*5	226	13	PE*8	112	80	242	2.5	46.8	61.6	14.8	2.9	Good	Very good	No abnormality			
Inv. Ex. 20	PET-IA*5	226	13	PP *7	168	85	226	2.5	47.5	67.2	19.7	4.5	Good	Good	No abnormality			
Inv. Ex. 21	2-layer PET*4	to 150	20	PP *7	168	20	207	2.5	19.7	24.9	5.2	8.9	Good	Very good	No abnormality			
Inv. Ex. 22	2-layer PET*4	to 150	20	PP *7	168	20	195	2.5	17.6	27.6	10	9.2	Good	Very good	No abnormality			
Inv. Ex. 23	2-layer PET*4	to 150	20	PP *7	168	20	183	2.5	15.8	31.6	15.8	9.6	Good	Very good	No abnormality			
Inv. Ex. 24	2-layer PET*4	to 150	20	PP *7	168	20	172	2.5	14.6	34.3	19.7	10	Good	Good	No abnormality			
Inv. Ex. 25	2-layer PET*4	to 150	20	PP *7	168	15	188	2.5	9.9	16.3	6.4	9.4	Good	Very good	No abnormality			
Inv. Ex. 26	2-layer PET*4	to 150	20	PP *7	168	15	178	2.5	8.8	20.1	11.3	9.8	Good	Good	No abnormality			
Inv. Ex. 27	2-layer PET*4	to 150	20	PP *7	168	15	168	2.5	6.9	25.9	19	12.5	Good	Good	No abnormality			
Inv. Ex. 28	PET*6	265	13	PP *7	168	90	285	2.5	58.7	66.8	8.1	1.6	Good	Very good	No abnormality			
Inv. Ex. 29	PET*6	265	13	PP *7	168	80	287	2.5	52.1	57.3	5.2	1.4	Good	Very good	No abnormality			
Inv. Ex. 30	PET-IA*5	226	20	PE*8	112	90	247	2.5	59.2	73.2	14	2.3	Good	Good	No abnormality			

Table 4

Table 4		Evaluation result																		
		Can outer surface side			Can inside surface side			Sheet temp- erature Ti °C	Speed v m/s	Speed					PET surface			Form- ability	Can inside surface whitening	Corrosion resistance after working*2
Material of film			MP1 (°C)	d1 (μm)	Material of film	MP2 (°C)	d2 (μm)			H21 %	H22 %	ΔH2 %	X-ray Ia/Ib*1							
Comp. Ex. 6	PET-PBT*3	214	12	PP *7	168	30	206	2.9	25.1	53.8	28.7	4.8		Poor	Poor	Medium corrosion				
Comp. Ex. 7	PET-PBT*3	214	12	PP *7	168	35	206	2.9	28.6	60.6	32	4.9		Poor	Poor	Medium corrosion				
Comp. Ex. 8	PET-PBT*3	214	12	PP *7	168	50	216	2.5	33.5	63.8	30.3	4.2		Poor	Poor	Small corrosion				
Comp. Ex. 9	PET-PBT*3	214	12	PP *7	168	40	206	2.5	31.2	55.3	24.1	5.2		Poor	Poor	Small corrosion				
Comp. Ex. 10	PET-IA*5	226	13	PP *7	168	90	226	2.5	49.8	72.3	22.5	4.8		Poor	Poor	Small corrosion				
Comp. Ex. 11	PET-IA*5	226	13	PE*8	112	80	226	2.5	43.6	68.7	25.1	4.3		Poor	Poor	Small corrosion				
Comp. Ex. 12	2-layer PET*4	to 150	20	PP *7	168	25	172	2.5	14.4	39.8	25.4	10.8		Poor	Poor	Large corrosion				
Comp. Ex. 13	2-layer PET*4	to 150	20	PP *7	168	20	150	2.5	13.8	49.6	35.8	12.5		Poor	Poor	Large corrosion				
Comp. Ex. 14	2-layer PET*4	to 150	20	PP *7	168	15	150	2.5	6.2	38.9	32.7	12.3		Poor	Poor	Large corrosion				
Comp. Ex. 15	PET-IA*5	226	13	PE*8	112	90	228	2.5	57.3	78.6	21.3	3.1		Poor	Poor	Small corrosion				

In these tables, "Good" in the formability column shows that no film damage could be recognized when performing the work of the later \*2, while "Poor" indicates that cracks accompanied with whitening were observed. "Very good" in the can inside surface whitening column indicates no whitening at all, "Good" indicates slight whitening of a substantially harmless extent, and "Poor" indicates that clear whitening was observed. Note that \*1 to \*8 in the evaluation columns of Table 3 and Table 4 indicate the same content as in Example 1.

\*1:  $I_a/I_b$  is the ratio of the following two peaks obtained by X-ray diffraction measurement using  $\text{CuK}\alpha$ -rays at a two-sided laminated metal sheet at the high melting point film (polyester film) covered side.  $I_a$  is the X-ray diffraction intensity by the diffraction face of the (100) face parallel to the surface of the polyester film (distance between faces about 0.34 nm), while  $I_b$  is similarly the X-ray diffraction intensity by the diffraction face of the (110) face (distance between faces about 0.39 nm). In the examples,  $I_a/I_b$  is 0.7 to 10 in range and shows that the crystal orientation remains without complete melting up to the surface layer.

\*2: The corrosion resistance after working is the result from punching a two-sided laminated metal sheet into a disk shape of a diameter of 158 mm, drawing it by a draw ratio of 1.56 so that the low melting point film becomes the inner surface to obtain a shallow drawn cup, then redrawing it by a draw ratio of 1.23 to obtain a can of a cup diameter of 82 mm and a cup height of 52 mm (DRD can), filling the inside with 2% citric acid, then storing it at 37 degrees for six months and examining the inside surface of the can for the state of corrosion.

\*3: PET-PBT is a mixed resin of polyethylene terephthalate and polybutylene terephthalate.

\*4: Two-layer PET is two-layer structure film with a surface layer of 10 $\mu\text{m}$  PET (MP 265°C) and a bottom layer of



10 $\mu$ m PET-IA (MP about 150°C).

\*5: PET-IA is polyethylene terephthalate/isophthalate copolymer.

\*6: PET is polyethylene terephthalate.

5 \*7: PP is polypropylene.

\*8: PE is polyethylene.

As clear from Table 3 and Table 4, the two-sided laminated metal sheets of the present invention where the difference  $\Delta H_z$  of the haze values of the low melting point film before and after bending is made 20% or less are superior in formability and corrosion resistance after working and are completely free of or exhibit almost no whitening when worked into a can or other container. As opposed to this, in the comparative examples where the difference  $\Delta H_z$  of the haze values before and after bending is over 20%, whitening is observed when worked into a container and the formability and corrosion resistance after working are also inferior, it is learned.

#### 20 INDUSTRIAL APPLICABILITY

In the laminated metal sheet according to the present invention, it is possible to adjust the thickness of the low melting point side film so as to simultaneously laminate two types of films with different melting points on the two sides of a metal sheet without sticking to the lamination rolls.

Further, even when bending the sheet to produce a food can etc., there is no whitening of the low melting point resin film and the inside of the can no longer appears to contain foreign matter. Further, if using for the high melting point film a biaxially stretched polyester-based resin film and leaving crystal orientation at that surface layer, the high melting point film can be given sufficient hardness or strength and the film thickness can be made thinner and the cost further reduced.

For this reason, there is the advantage that existing lamination apparatuses can be used as they are.